

# **Total Mercury Monitoring Procedures For Meeting WPDES Permit Requirements (For Permittees)**

## **5/21/03**

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### **General Precautions**

Mercury poses special problems in regulating its release to the environment. Its presence at even very low concentrations in surface water can cause it to accumulate in fish, causing health problems for humans and other mammals who consume those fish. In November 2002, DNR implemented a special regulatory approach under the WPDES program for mercury that acknowledges the special challenges with regulating a substance that causes problems at such low levels. Section NR 106.145, Wisconsin Administrative Code contains the main framework for that new regulatory approach.

Persons required to perform mercury analysis by their wastewater permits must use an extremely sensitive test method that can be affected by even slight contamination not related to the mercury level in the wastewater. This contamination of samples or sample containers may originate from the air, sampling personnel or contacted surfaces. To avoid this contamination and to properly collect clean samples for mercury analysis, you should have a team of at least two people with a good understanding of potential sources of contamination. The team should follow the "clean hands/dirty hands" technique referenced in s. NR 106.145(9), Wis. Adm. Code and described below (excerpted from EPA *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*). This technique is also demonstrated in the EPA video *Sampling Ambient and Effluent Waters for Trace Metals*.

Because even slight contamination can adversely affect effluent or background sample results, the new rule contains some requirements that are unique to Wisconsin's toxic substances regulatory program. For example, each day you collect samples, you must generate and analyze a field blank. A field blank is a portion of mercury-free water that is processed through the full sequence of sampling steps (s. NR 106.145(9), Wis. Adm. Code).

You can grab a sample by dipping the sample bottle directly into the water stream to be sampled or holding the bottle under a flowing spigot. If it becomes necessary, for safety or logistical reasons, to use a sampling pole to allow reaching a water stream, take precautions to thoroughly clean any surfaces of the sampling apparatus that will contact the sample bottle.

EPA Method 1669 is performance-based. This means that less stringent procedures may be used as long as contamination levels are maintained at acceptable levels. S. NR 106.145(9) specifies the acceptable contamination as a percentage of sample mercury concentrations. Therefore, somewhat higher levels of sample contamination are acceptable for POTW influent samples, which will often be collected using automatic samplers that are subject to more contamination.

Similarly, less sensitive laboratory test methods may be used for samples having higher mercury concentrations, such as influent samples.

Persons wishing more information might visit the DNR web site at <http://www.dnr.state.wi.us/org/water/wm/ww/mercury/mercury.htm>. Information available includes links to the Wisconsin Administrative Code, pollutant minimization program materials and other low-level mercury monitoring information including EPA Methods 1631 (testing) and 1669 (sampling).

### **Contracting with a Laboratory**

To meet the requirements of s. NR 106.145(10), Wis. Adm. Code, the laboratory that conducts your mercury analyses:

- Must be Wisconsin-certified and must be recognized for low level mercury capability
- Must have a limit of quantitation (LOQ) at or below the level in your sample or 1.3 ng/L, whichever is greater. We expect effluent and intake samples to generally fall in the 1 to 10 ng/L range.
- May use a less sensitive method for POTW influent samples. POTW influent levels are commonly in the 50 to 200 ng/L range.

Arrangements that should be made ahead of time:

- Discuss with the lab what supplies you need them to provide (correct number of double-bagged sample bottles, mercury-free water for blanks or rinsing, plastic or non-talc latex gloves, other cleaned equipment) or what you should obtain yourself.
- Determine a means of shipping your samples that is convenient for you and the lab.

Pursuant to s. NR 106.145(10)(d), you must contract with a laboratory that is certified under ch. NR 149 for low-level mercury analyses, or a lab that has been certified under ch. NR 149 for mercury and recognized by the Department as having low-level mercury capabilities under the emerging technology provisions of s. NR 149.12(2). As of May 15, 2003, the labs listed below are recognized under s. NR 149.12(2). The locations, phone numbers and approximate LOQs are also listed. For list updates, including deletions and additions, consult [http://www.dnr.state.wi.us/org/es/science/lc/info/Hg\\_low.htm](http://www.dnr.state.wi.us/org/es/science/lc/info/Hg_low.htm).

| <u>Laboratory Name</u>   | <u>City and state</u> | <u>Phone number</u> | <u>Approx. LOQ</u> |
|--------------------------|-----------------------|---------------------|--------------------|
| Northern Lake Service    | Crandon, WI           | (715) 478-2777      | 0.2 ng/L           |
| S-F Analytical           | Milwaukee, WI         | (800) 300-6700      | 50 ng/L            |
| En Chem                  | Kimberly, WI          | (920) 469-2436      | 0.5 ng/L           |
| Frontier Geosciences     | Seattle, WA           | (206) 622-6960      | 0.2 ng/L           |
| Battelle Marine Sciences | Sequim, WA            | (360) 681-3650      | 0.5 ng/L           |
| Brooks Rand LTD          | Seattle, WA           | (206) 632-6206      | 0.5 ng/L           |
| North Shore Analytical   | Duluth, MN            | (218) 729-4658      | 0.3 ng/L           |

## **Supplies and Equipment Recommended**

- A shipping container for the sampling event to identify and protect bottles
- The correct quantity of properly cleaned and prepared glass or fluoropolymer (teflon®) bottles (polyethylene bottles should not be used), stored in double self-seal plastic bags (remember blank and extra bottles, if glass, to account for breakage)
- Lab water, for blanks, in containers and sealed in plastic bags
- Provision for labeling samples (pre-labeled outer bags or other method)
- A sampling table and clean plastic sheeting to cover the table top and plastic clamps or other provision for retaining the plastic sheet on the table (the table may not be necessary if you don't have to set down bottles or you may set them down on another plastic-covered surface)
- Data log book and lab sheets or chain of custody sheets
- Personal protective equipment that you would normally use when collecting samples at the sample collection site
- Tyvek® (or equivalent) coveralls for sampling personnel (unnecessary if you are able to collect uncontaminated samples without them)
- Clean sampling pole stored in protective covering with a detachable piece (preferably plastic and previously cleaned and stored in a plastic bag) that may be used to securely hold the sample bottle (not necessary if you are able to dip the sample bottle directly into the water to be sampled)

## **Sampling Locations**

If possible, select a location where the sample can be grabbed by dipping the sample bottle directly into the water stream to be sampled. If it becomes necessary, for safety or logistical reasons, to use a sampling pole to allow reaching a water stream, make the necessary provisions for securing the sample bottle to the pole in such a way as to avoid contamination of the outside of the bottle. Sampling teams have used various inventions that compliment the clean hands/dirty hands procedure. Your laboratory or DNR contact may be able to suggest a set-up that will work for your situation.

To minimize cross-contamination, collect the field blank first and then the cleanest sample and finally the dirtiest sample. Change gloves in between.

- Effluents and intake samples should be grab samples
- You may collect intake samples (for industrial facilities whose water supply is withdrawn from the receiving water) directly up-river to the intake structure or at an in-plant structure prior to use or potential contamination. If ice cover creates problems with obtaining sample, contact your DNR representative to work out a mutually acceptable solution.
- You may sample chlorinated effluents at a point before or after chlorination.
- You should collect a POTW influent sample as an aliquot from the composite sampler bottle.

## **Sample Collection**

Attachment 1 shows step-by-step mercury sample and field blank collection procedures.

## Preservation and Storage for Total Mercury

Ship collected samples to the lab following the procedures you and your lab agreed to.

- Refrigeration of samples for total mercury analysis is not required. In very cold weather, prevent the samples from freezing such as by shipping overnight.
- Follow the instructions of your laboratory for chemical preservation, if any. Preservation of samples in the field is optional. The Department recommends omitting field preservation, thereby eliminating that step as a potential source of contamination.

*Note: Sample bottles that contain acid preservative may need to be shipped in accordance with the federal hazardous materials rules (49 CFR, Part 172).*

## Reporting Data to DNR

Data for total mercury for all sample locations and grab sample field blanks must be reported to the Department on Discharge Monitoring Reports (DMRs). Limit of detection (LOD) and limit of quantitation (LOQ) values reported to you by your lab must also be reported on the DMR. The value reported in the field blank column on the DMR should be the one generated by the grab field blank procedure. See the attachment for discussion of influent field blanks.

Pursuant to ss. NR 106.145(9) and (10), labs must report results of both field blanks and method blanks on reports sent to clients. Labs may correct reported sample results based on method blank concentrations if criteria are met and clearly shown on reports. Labs or permittees **may not** correct sample results by subtracting results of field blanks.

## Future Sample Quality Improvement

S. NR 106.145(10)(b), Wis. Adm. Code requires that the analytical method used for a sample must be sensitive enough to quantify actual mercury concentrations in the sample, or down to 1.3 ng/L, whichever is greater. If a sample result is greater than 1.3 ng/L but falls below the LOQ that your lab reported, your lab did not use a sensitive enough method. If that happens, your lab should retest the sample using a more sensitive method. If your lab is unable to perform a more sensitive method, the lab should subcontract to a lab capable of meeting the necessary sensitivity. If you are unable to acquire data that meets these requirements for any monitoring period, we recommend that you report the sample result with the LOD and LOQ from the less sensitive method on the DMR and then contact another lab to perform future analyses.

S. NR 106.145(9)(c), Wis. Adm. Code requires that field blank sample results must not exceed a) one-fifth the level in the sample, b) the test LOD or c) 0.5 ng/L, whichever is greatest. If results of the monitoring reported by the lab indicate higher field blank contamination, you should still submit the results of samples and field blanks, as reported by your lab, on the DMR. However, for future monitoring events, take steps to reduce contamination by investigating potential sources of contamination and taking corrective steps on your sampling procedures.

If you have questions, contact your lab or your DNR representative or Tom Mugan at (608) 266-7420 or Donalea Dinsmore at (608) 266- 8948.

## **Attachment 1 - Clean Hands/Dirty Hands Basic Sampling Procedure Excerpted from EPA Method 1669**

### **Recommended Step-by-step Procedure**

This is the basic procedure for collecting one sample. It should give sampling personnel an idea on which surfaces each person on the team may touch. To incorporate collection of field blanks into the procedure you may add a third person (another clean hands) to the team or you may try a procedure where "Clean hands" sets sample bottles down on previously spread plastic sheeting. Descriptions of possible field blank procedures follow the basic procedures for collecting samples.

1. Both members of the team carry the equipment near to the sampling site.
2. Both members remove Tyvek® suits from protective bag and put them on (if used).
3. Designate one member of the team as "clean hands" and the other as "dirty hands".
4. "Dirty hands" opens a bag containing non-talc gloves.
5. "Clean hands" removes a pair of clean gloves and puts them on. "Clean hands" touches only the inner bag and sample bottle from this point on.
6. "Dirty hands" removes a pair of clean gloves and puts them on.
7. "Dirty hands" removes an empty bagged sample bottle from the shipping container (and closes the container) and opens the outer bag.
8. "Clean hands" opens the inner bag, removes the bottle, and folds down the inner bag.
9. "Dirty hands" seals the outer bag and puts it back in the shipping container.
10. "Clean hands" removes the bottle cap and holds the cap in one hand.
11. With the other hand, "Clean hands" fills the sample bottle by dipping into the flowing water stream, taking care to keep their hand "downstream" of the inlet of the sample bottle. The bottle is filled, leaving a slight headspace. "Clean hands" tightly screws the cap back onto the bottle.
12. "Dirty hands" retrieves the bags and opens the outer bag.
13. "Clean hands" reaches inside to re-open the inner bag, puts the sample bottle inside and seals the inner bag.
14. "Dirty hands" seals the outer bag and places the bagged sample into the shipping container.
15. One member of the team then records the sample bottle number with description and other relevant data.

### **Field Blank Collection Procedures**

Again, it may be useful to use a third person (another "clean hands") for field blank collection. Alternatively, the "Clean hands" person may set sample bottles or field blank bottles down on previously spread, clean plastic sheeting. The grab field blank procedures check for contamination using sampling procedures for grab procedures that are used for effluent samples or (for industrial facilities) intake samples. Report results of the grab sample field blank on the Discharge Monitoring Report each time you report grab sample results.

*Note: A field blank is a volume of mercury-free water (usually shipped from the lab) that is processed through the full sequence of sampling steps. Contrast this to a trip blank that is a bottle that "goes along for the ride" but remains unopened at the sampling site.*

**Possible grab field blank procedure #1** uses a procedure where sample bottles come from the lab filled with mercury-free water. Once "Clean hands" retrieves a full sample bottle from the inner bag, "Cleans hands" pours the contents out to waste and sets the bottle and cap on the plastic sheeting. "Clean hands" then retrieves a second full bottle from its inner bag, removes the cap and pours its contents into the first bottle. The first bottle now becomes the field blank and is repacked into its double bag. The second bottle that has been emptied is now used to collect the sample according to the above procedure.

**Possible grab field blank procedure #2** uses a large double-bagged container of mercury-free water supplied by the lab. After opening the field blank bottle outer bag for "Clean hands", "Dirty hands" seals and temporarily stores the outer bag. "Dirty hands" then retrieves the filled large water bottle and opens the outer bag while supporting the bottle. "Clean hands" removes the cap from the field blank bottle and sets both on the plastic sheeting and then opens the inner bag of the large water bottle, removes the lid and exposes the mouth of the container so "Dirty hands" can pour from it. As "Dirty hands" pours, "Clean hands" picks up the field blank bottle and collects the field blank. "Clean hands" caps the field blank bottle, sets it on the plastic sheeting then recaps the large water bottle and seals the inside bag. "Dirty hands" then seals the outer bag, returns the large bottle to the shipping container, retrieves the double bag for the field blank bottle and reopens the outer bag for "clean hands" to replace the field blank.

**Composite sampler field blank procedures** may be appropriate when a permit requires a POTW to collect influent composite samples. Since a field blank is processed through the entire sampling procedure, a composite sampler field blank (used for influent) will not be the same as an effluent grab sample field blank (used for effluent). You report results of the **grab sample** field blank on the Discharge Monitoring Report each time that you report grab-sample results. Assessing influent sample contamination is more appropriately done as part of the pollutant minimization program documentation required by NR 106.145(7).

The sampling equipment and sample collection container should be cleaned and the tubing should be replaced regularly. Because influent levels of mercury typically exceed 50 ng/L, you can expect any bias imparted by ambient contamination to be overwhelmed by the sample concentration. The logistical barriers of collecting a field blank through the composite sampler may be difficult enough to overcome that it may be necessary to devise other means of assessing contamination in these samples. For example, comparing a grab sample with a sample "grabbed" simultaneously by the automatic sampler might provide an indication of the level of contamination introduced by the sample coming in contact with sampler lines, piping, sub-samplers or composite containers

If you do collect a composite sampler field blank, you will need a large container of mercury-free water like the one described in grab field blank procedure #2. Since there are different types of samplers in use, procedures will vary with the sampler type. For suction tube samplers, draw a volume of mercury-free water out of a storage vessel, through the tubing and pump and into the composite container. For flow-through samplers, you will need to devise a way to transfer some of the mercury-free water into the sub-sampler mechanism. Once the blank water is in the composite container, use clean hands/dirty hands procedures to transfer a mixed (such as by swirling) aliquot into the field blank bottle.